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Published in:
Surface & Coatings Technology

DOI:
[10.1016/j.surfcoat.2016.12.001](https://doi.org/10.1016/j.surfcoat.2016.12.001)

Published: 25/06/2017

Document Version
Peer reviewed version

[Link to publication on the UWS Academic Portal](#)

Citation for published version (APA):

Mazur, M., Howind, T., Gibson, D., Kaczmarek, D., Morgiel, J., Wojcieszak, D., Zhu, W., & Mazur, P. (2017). Modification of various properties of HfO₂ thin films obtained by changing magnetron sputtering conditions. *Surface & Coatings Technology*, 320, 426-431. <https://doi.org/10.1016/j.surfcoat.2016.12.001>

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Accepted Manuscript

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PII: S0257-8972(16)31289-0
DOI: doi: [10.1016/j.surfcoat.2016.12.001](https://doi.org/10.1016/j.surfcoat.2016.12.001)
Reference: SCT 21858
To appear in: *Surface & Coatings Technology*
Received date: 22 August 2016
Revised date: 29 November 2016
Accepted date: 1 December 2016

Please cite this article as: Michal Mazur, Torsten Howind, Des Gibson, Danuta Kaczmarek, Jerzy Morgiel, Damian Wojcieszak, Wenzhong Zhu, Piotr Mazur , Modification of various properties of HfO₂ thin films obtained by changing magnetron sputtering conditions. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Sct(2016), doi: [10.1016/j.surfcoat.2016.12.001](https://doi.org/10.1016/j.surfcoat.2016.12.001)

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Modification of various properties of HfO₂ thin films obtained by changing magnetron sputtering conditions

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Abstract

In this work properties of hafnium dioxide (HfO₂) thin films deposited by magnetron sputtering with different powers (i.e. 200 W, 400 W and 600 W) were described. Based on microstructure measurements obtained by X-ray diffraction, Raman scattering and transmission electron microscopy method it was observed that there is a significant influence of the sputtering power on investigated properties of HfO₂ thin films. Increase of the sputtering power caused, e.g. an increase of average crystallite size and surface roughness. Microstructure of thin films deposited with lower power was composed from a large number of voids that resulted in significant changes of their optical and mechanical properties. Results of optical studies showed that all deposited thin films were well transparent in a visible light range. Refractive index increased gradually with an increase of deposition power from 1.86 (200 W) to 2.09 (600 W). Performed investigations of mechanical properties revealed that hardness and Young's elastic modulus of HfO₂ thin films increased with an increase of the sputtering power.

Keywords: HfO₂, thin films, magnetron sputtering, microstructure, optical properties, mechanical properties

Introduction

Nowadays, thin oxide films with precisely controlled properties are desired for the development of modern technologies. One of such oxide is hafnium dioxide (HfO₂), which is characterized by a very good thermal, chemical, mechanical stability and high transparency over the wide wavelength range [1-3]. HfO₂ exhibits low optical absorption and dispersion, high refractive index, high dielectric constant ($k \sim 25$) and wide band gap ($E_g \sim 5.7$ eV), which makes it an attractive material for many applications in the fields of electronics and opto-electronics [4]. For example thin films based on HfO₂ are used as optical filters, ultraviolet heat mirrors, antireflection coatings and in space applications [5,6]. Amorphous HfO₂ thin films can be used in flexible thin film capacitors, computer memory elements, optical coatings for polymer substrates or fiber optic waveguides. Due to its low absorption in UV region HfO₂ can be also considered as high index material for high laser damage coatings [4]. In the field of electronics it is a leading candidate to replace SiO₂ dielectrics in gate oxides due to high permittivity and low electron tunneling effect [4]. According to the literature HfO₂ may be also applied as complementary metal-oxide-semiconductor devices, memory or magnetoelectronic devices [7]. In recent years it has also attracted a lot of attention due to its possible application in resistive random access memories [8,9] and therefore it can be perceived as a potential smart material. According to mentioned excellent optical and electrical properties, HfO₂ thin films are envisioned as a promising candidate for the optical information storage [8].

However, properties of HfO₂ thin films strongly depend on the preparation method and deposition conditions. Therefore in this paper, the influence of sputtering power of HfO₂ thin films on their structural, surface, optical and mechanical properties has been thoroughly investigated.

Experimental

HfO₂ coatings were prepared by magnetron sputtering (MS) using metallic Hf targets of high purity [10,11]. Thin films were sputtered in pure oxygen, without argon as a working gas. Three sets of thin films were prepared using various sputtering power, i.e. 200 W, 400 W and 600 W. The distribution of the power supplied to magnetron was precisely controlled due to application of a special control system that is managing the work of MSS2 (DORA Power System) pulsed DC power supply units. The distance between the target and substrates was equal to 80 mm and a time of sputtering was equal to 90 minutes. The base pressure in the deposition chamber was ca. $5 \cdot 10^{-5}$ mbar, while during the sputtering process it was equal to $2 \cdot 10^{-2}$ mbar. Thin films were deposited on unheated silicon and fused silica substrates with a size of 20x20 mm².

Structural properties of as-prepared thin films were determined by several methods, i.e. x-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy. Siemens 5000 powder diffractometer with Cu K α X-ray ($\lambda=1.54056$ Å) was used and the crystallite sizes were calculated using Scherrer's equation [12]. Raman spectra were measured using a Thermo Scientific DXR™ Raman Microscope instrument equipped with a CCD camera detector. The spectra were recorded in the range from 70 to 800 cm⁻¹ with a resolution of <1 cm⁻¹ and the spot size had a diameter of 1.8 µm. The excitation source was a 455 nm blue laser diode at a power of 8 mW. 10 scans were performed for each sample with the exposure time of 90 s. The crystal structure of the HfO₂ thin films was also characterized by a TECNAI G² FEG Super-Twin (200 kV) transmission and scanning electron microscope fitted with a high angle annular dark field (HAADF) detector. Additionally, the local chemical composition was analyzed with an integrated X-ray energy dispersive attachment (EDS) with an EDAX UTW detector.

Surface topography and roughness was determined with the aid of UHV VT AFM/STM Omicron atomic force microscope (AFM) operating in ultra-high vacuum conditions in a contact mode. X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the oxidation states on the sample surface applying a Specs Phoibos 100 MCD-5 hemispherical analyzer using a

Specs XR-50 X-ray source with Mg K α (1253.6 eV) beam. All spectra were calibrated with respect to the binding energy of adventitious C1s peak at 284.8 eV.

Optical properties of as-prepared thin films were determined based on transmittance and reflectance measurements obtained using Aquila nkd-8000 spectrophotometer. Spectra were recorded at 30 degrees angle of incident light for both S and P light polarisation and refractive index characteristics of the films were determined by reverse engineering method. Additionally porosity and packing density of deposited thin films were analyzed.

Mechanical properties, i.e. hardness and Young's modulus, were evaluated by a Keysight Nano Indenter G200 fitted with a Berkovich indenter tip. The micro-mechanical property values of each film were determined by traditional load-controlled nanoindentation testing and continuous stiffness measurements (CSM). In the case of each sputtered thin film 5 indentation measurements using traditional nanoindentation and CSM method were performed in various areas of a coating. To determine the hardness and the elastic modulus from the load-displacement data obtained from nanoindentation experiments the Oliver and Pharr method was used [13].

Results and discussion

The XRD patterns of HfO₂ thin films deposited with different sputtering powers are shown in Fig. 1a. All hafnium dioxide coatings had nanocrystalline structure of monoclinic phase. Thin films deposited at lower powers of 200 W and 400 W were textured among (002) crystal plane, while coating sputtered at 600 W was strongly textured among (-111) crystal plane. It was observed that with an increase of sputtering power the diffraction peaks had significantly more intensive peaks which could testify about more crystalline structure. In contrast, broadening and low intensity of diffraction peak obtained for HfO₂ thin film sputtered at 200 W or 400 W can indicate on appearance of a large amount of amorphous phase. XRD studies also revealed that an increase of deposition power caused an increase of crystallite sizes from 6.5 nm for HfO₂ deposited at 200 W up to 21.4 nm for film sputtered at 600 W.

Raman scattering used for structural analysis is very sensitive to crystallinity and microstructure of thin films. Therefore, this method was used for further analysis of structural properties of deposited thin films. In the case of HfO_2 thin films with monoclinic structure the theoretical group predicted that it possesses 18 active modes ($9A_g$ and $9B_g$) [14-16]. The peaks in Fig. 1b of as-prepared hafnium dioxide are in good agreement with the reference values, indicating that deposited thin films had monoclinic phase. Peaks observed at 108, 133, 147, 254, 379, 496, 578 and 671 cm^{-1} can be assigned to the A_g modes, while peaks found at 164, 241, 335, 396, 519, 549, 639 and 778 cm^{-1} corresponds to the B_g modes of monoclinic HfO_2 phase, respectively [14]. The strongest and sharpest peaks were observed for thin films deposited with a power of 600 W, which can indicate that this coating had the most crystallized structure. The decrease of deposition power resulted in the gradual weakening and broadening of Raman lines that could testify about less crystallized microstructure or more amorphous character of the coatings.

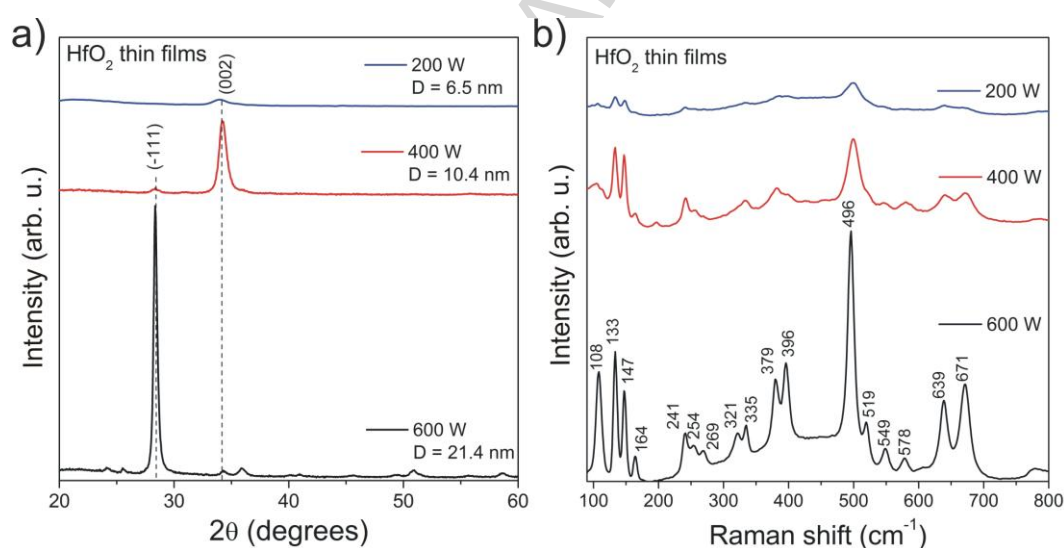


Fig. 1. Microstructure investigation results obtained by: a) XRD and b) Raman spectroscopy for HfO_2 thin films prepared with various sputtering power. Designations: D – crystallite size

XRD and Raman studies confirmed that the change of the deposition power of HfO_2 thin films strongly affects their growth mechanism, which has a direct impact on their microstructure. Therefore, transmission electron microscopy was also used to analyze the structural properties of prepared thin films. Microstructure observations in the bright field mode (BF TEM) of HfO_2

coating deposited with 200 W sputtering power (Fig. 2a) revealed that it had fine-crystalline structure, however it was composed from a large number of voids. The analysis of electron diffraction (attached as insets to the bright field images in Fig. 2) confirmed that the nanocrystalline phase in the thin films is of HfO₂ monoclinic crystal lattice. Selected area electron diffraction (SAED) pattern had almost spotted character that can indicate occurrence of very strong texture in this coating. In the case of HfO₂ thin films deposited with 400 W sputtering power (Fig. 2b) the bright field image revealed similar character of the microstructure as-compared to sample deposited with 200 W. However, in this case the number of voids was lower and their size were usually smaller. In turn, for thin films deposited with the highest power of 600 W the change of microstructure was clearly visible. The structure had coarse crystalline and columnar character (boundaries between the columns are marked in Fig. 6c with a dotted line). Columns were free of defects, which also did not occur in their boundaries. The growth of columns started from the substrate and their width is large of even 50-80 nm. In this case SAED pattern had spotted character, which testify about highly crystalline microstructure of the sample and that its crystallite sizes are rather of large sizes. Analysis of SAED pattern revealed that coating had HfO₂ monoclinic phase of [001] zone axis.

In order to precisely determine the structure of deposited thin films, high resolution transmission electron microscope (HRTEM) studies were also performed. These measurements confirmed that prepared thin films with various sputtering powers consisted of a fine nanocrystalline structure with HfO₂ monoclinic phase. The HRTEM images with FFT diffraction patterns are shown in Fig. 2 as insets. FFT diffraction patterns were obtained from the crystallites free of defects, which allowed for more accurate evaluation of the plane separation values and their angles than measured directly from high resolution images.

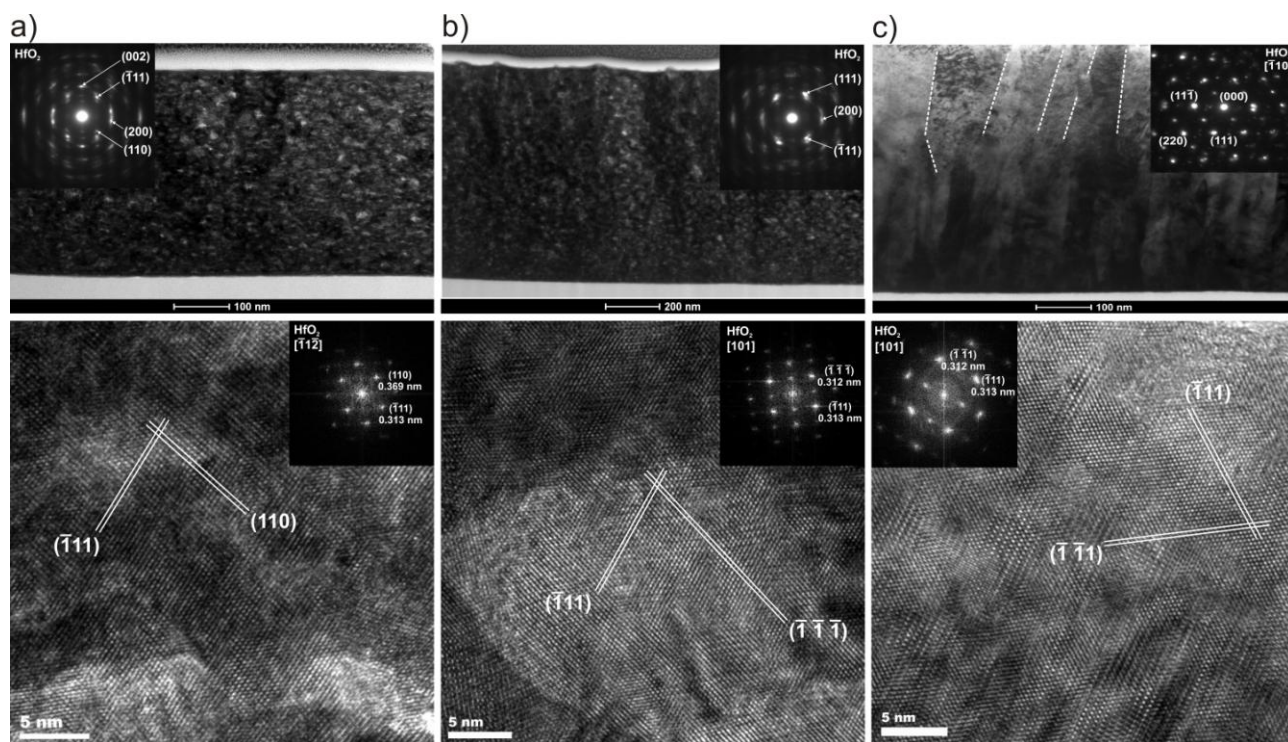


Fig. 2. Bright field and HRTEM images of the cross section of as-deposited HfO_2 thin films deposited by pulsed DC MS with different power: a) 200 W, b) 400 W and c) 600 W

Presence of the voids in thin films deposited with powers of 200 W and 400 W indicated that the concentration gradient of elements could appear. Therefore, the concentration of material components, i.e. Hf and O as a function of the thin film depth was also determined. Voids were marked in the BF TEM image (Fig. 3a) and closely shown in HRTEM image (Fig. 3b). The size of the voids is in the range from ca. 10 nm to 50 nm. The STEM image of the cross-section of thin films with marked line of the EDS profile scan of Hf and O components is shown in Fig. 3c. Two cross-sections were performed in order to show the change of material composition in the chosen void (1st line) and through entire thin film (2nd line). EDS profile scan of a chosen void showed non-homogenous profile of material composition and that in the void area there is only change of hafnium concentration, while oxygen content is rather stable. This could indicate that voids were composed from oxygen. Line scan through an entire thickness of HfO_2 thin film confirmed that in the voids areas there was a change of hafnium concentration and the oxygen content was stable.

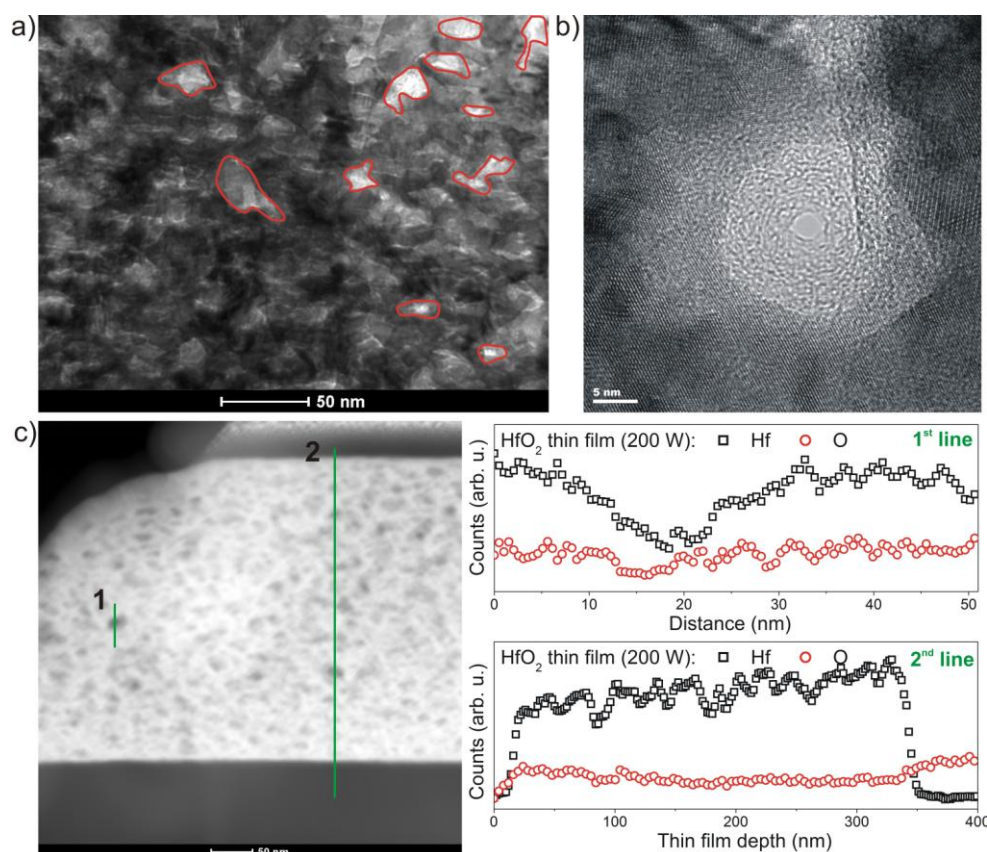


Fig. 3. TEM investigation results: a) BF TEM image with marked voids, b) HRTEM image of void and c) STEM image with marked lines of EDS depth profiles analysis of HfO_2 thin films deposited with a power of 200 W

Three-dimensional AFM images are shown in Fig 4a-c. In the case of all HfO_2 thin films their surface was densely packed, crack-free and homogenous. With the increase of the sputtering power from 200 W to 400 W and 600 W, the maximum height of the surface profile also increased from ca. 5.3 nm, 11.0 nm to 33.0 nm, respectively. The height distribution of as-prepared coatings are presented in Fig. 4 as insets in AFM surface images. In all cases results showed a symmetric height distribution in the samples which can testify about good homogeneity of the surface. Root mean square (RMS) surface roughness increased with the increase of thin films deposition power and was equal to 1.0, 1.9 and 6.0 nm for coatings prepared with sputtering powers of 200 W, 400 W and 600 W, respectively. Surface cross-section (Fig. 4d) confirmed that with the increase of sputtering power the roughness of thin films also increased. XPS studies indicated that at the surface of prepared thin

films only Hf^{4+} oxidation state occurred, which revealed that the surface was fully oxidised due to the position of $\text{Hf}4f$ doublet and the separation energy width equal to 1.65 eV between $\text{Hf}4f_{7/2}$ and $\text{Hf}4f_{5/2}$ peaks (Fig. 4e). Therefore, it testified about the formation of HfO_2 [17]. In turn, results obtained for $\text{O}1s$ oxidation state (Fig. 4f) showed that in case of all deposited samples their surface had ability to adsorb water molecules and hydroxyl radicals.

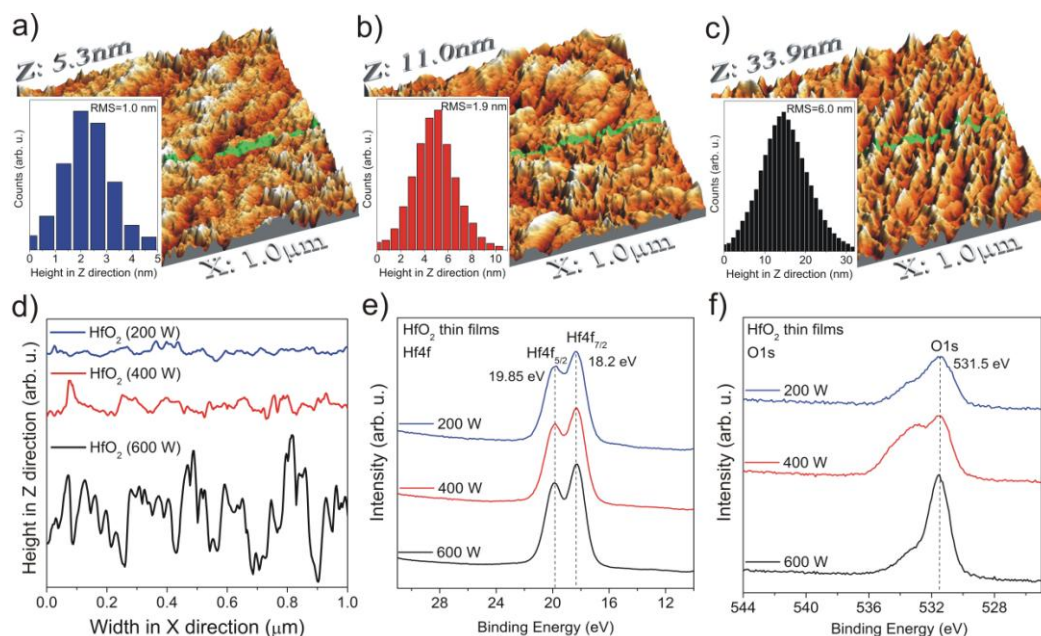


Fig. 4. Surface measurements results of HfO_2 thin films prepared by magnetron sputtering with various deposition power: 3D images of the surface of coatings sputtered at a) 200 W, b) 400 W, c) 600 W, d) cross section of the surface, e) XPS spectra of $\text{Hf}4f$ and f) $\text{O}1s$ core levels

HfO_2 thin films were well transparent in the measured wavelength range. The transmittance and reflectance spectra are shown in Fig. 4a-c. Based on these results refractive index was determined using reverse engineering method with the aid of Cauchy dispersion model with 5 oscillators and Powell's analysis method. Calculations were performed using Pearson's test – χ^2 (Chi-square). Results (Fig. 5d) showed that with the increase of sputtering power the refractive index also gradually increase from 1.86 (for films deposited at 200 W) to 2.09 (for films deposited at 600 W). Based on obtained values, porosity (P) and packing density (PD) were calculated using following equations [18,19]:

$$P(\%) = \left[1 - \left(\frac{n_f^2 - 1}{n_b^2 - 1} \right) \right] \cdot 100\% \quad (1)$$

$$PD = \frac{(n_f^2 - 1) \cdot (n_b^2 + 2)}{(n_f^2 + 2) \cdot (n_b^2 - 1)} \quad (2)$$

where: n_f – measured refractive index of thin film, n_b – refractive index of the bulk material.

Values of refractive index for bulk HfO_2 with monoclinic phase is equal to 2.12 [20] and it is slightly higher than for thin film deposited with 600 W sputtering power. The highest porosity (Fig. 5e) of 29.4% was obtained for thin film deposited with the lowest power of 200 W. With the increase of deposition power to 400 W and 600 W porosity decreased to 16.2% and 3.3%, respectively. The values of packing density (Fig. 5e) were inverse that means the highest value of 0.98 was obtained for thin film deposited with a power of 600 W. Decrease of the sputtering power to 400 W and 200 W resulted in a decrease of packing density to 0.94 and 0.84, respectively. Therefore, it can be assumed that thin films deposited with a highest power exhibit the most closely packed structure.

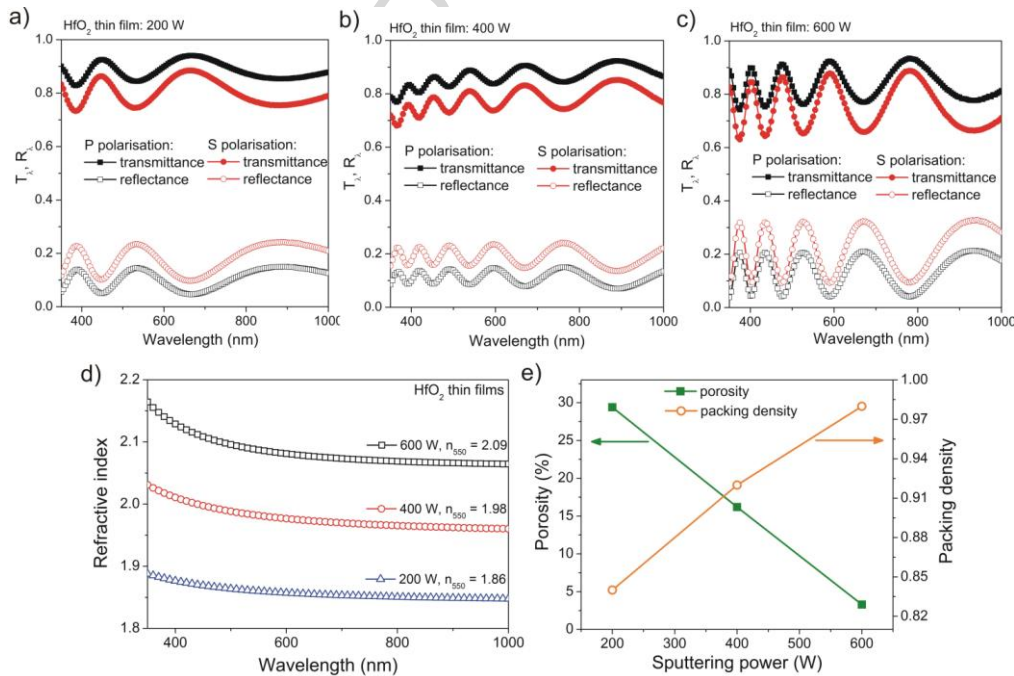


Fig. 5. Transmittance and reflectance spectra obtained for S and P polarization and 30 degrees of light incidence for HfO_2 thin films deposited with various power: a) 200 W, b) 400 W, c) 600 W, d) comparison of their refractive index characteristics and e) porosity and packing density

In order to determine hardness and elastic modulus of deposited HfO_2 thin films nanoindentation measurements were performed. Results of the mean hardness-displacement and elastic modulus-displacement curves measured by CSM technique are shown in Fig. 6. HfO_2 thin film deposited with 600 W sputtering power exhibited the highest hardness of ca. 12.0 GPa and elastic modulus of ca. 147.4 GPa. In turn, thin film deposited at 400 W revealed hardness of 7.9 GPa and elastic modulus of 119.2 GPa. Further decrease of the sputtering power to 200 W resulted in a decrease of hardness to 4.9 GPa and elastic modulus to 82.4 GPa. Such results may lead to the conclusion that the increase of sputtering power was favourable for the hardness of deposited coatings. As it was shown by TEM studies and optical measurements, the introduction of voids caused increase of the porosity and decrease of packing density of thin films. Therefore, the less dense thin film is the lower hardness could be obtained. Results determined by conventional nanoindentation and CSM technique are summarized in Table 2. It is worth to emphasize that results obtained by both techniques were very similar, which seems to confirm that measurements were performed correctly.

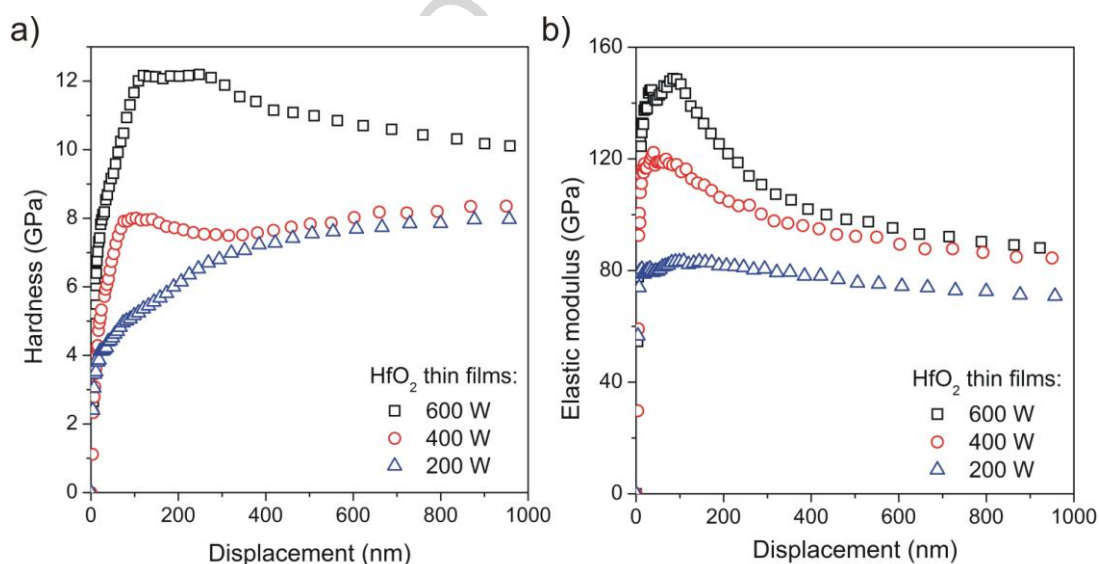


Fig. 6. Average values of: a) hardness and b) elastic modulus of HfO_2 thin films in a function of penetration depth

Table 1. Hardness and elastic modulus of deposited HfO₂ thin films

Thin film:	HfO ₂ (200 W)	HfO ₂ (400 W)	HfO ₂ (600 W)
Conventional nanoindentation testing	$H = 5.0 \pm 0.3$ GPa	$H = 8.0 \pm 0.4$ GPa	$H = 11.7 \pm 0.3$ GPa
	$E = 88.7 \pm 5.1$ GPa	$E = 121.2 \pm 4.2$ GPa	$E = 156.9 \pm 7.1$ GPa
Continuous Stiffness Measurement (CSM)	$H = 4.9 \pm 0.3$ GPa	$H = 7.9 \pm 0.1$ GPa	$H = 12.0 \pm 0.2$ GPa
	$E = 82.4 \pm 0.8$ GPa	$E = 119.2 \pm 2.4$ GPa	$E = 147.4 \pm 2.5$ GPa

Summary

In this work three sets of HfO₂ thin films were prepared using magnetron sputtering with various deposition powers, i.e. 200 W, 400 W and 600 W. Deposition conditions had significant impact on microstructure, surface, optical and mechanical properties of manufactured coatings.

With the increase of deposition power the average size of crystallites increased from 6.5 to 21.4 nm. All thin films were nanocrystalline, however those deposited at lower powers contained a large number of voids composed of oxygen, which were confirmed by TEM and EDS studies. AFM measurements showed homogenous surface of all thin films, while with the increase of sputtering power the RMS surface roughness increased from 1.0 to 6.0 nm. Due to the XPS studies results it was found that surface was fully oxidized and it had ability to adsorb water molecules and hydroxyl radicals. Transparency of deposited thin films was high (above >80%), while sputtering power influenced on refractive index and therefore on porosity and packing density of coatings. With the increase of deposition power refractive index increased from 1.86 to 2.09, porosity decreased significantly and packing density increased. Mechanical properties were also dependent on sputtering power. With the increase of deposition power hardness increased from ca. 4.9 GPa to ca. 12.0 GPa and elastic modulus increased from 82.4 GPa to 147.4 GPa.

Taking into consideration obtained results it can be assumed that by the change of deposition power of HfO₂ thin films one can precisely control its microstructure, surface, optical and mechanical properties.

Acknowledgments

This work was financed from the sources given by the Polish National Science Centre NCN in the years 2014-2017 as a research project No. DEC-2013/09/B/ST8/00140.

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Highlights

1. HfO₂ thin films were deposited using magnetron sputtering with various powers
2. Deposition conditions had significant impact on the properties of deposited coatings
3. Increase of sputtering power caused increase of crystallite sizes from 6.5 to 21.4 nm
4. Sputtering power influenced on refractive index, porosity and packing density
5. With the increase of deposition power hardness increased from 4.9 GPa to 12.0 GPa